# SYNOPSIS

## SYNTHESIS, CHARACTERISATION AND UTILISATION OF WATER SOLUBLE POLYVINYL ALCOHOL-SELECTED AMINO ACID COMPOSITES AS CORROSION INHIBITORS FOR MILD STEEL IN ACID MEDIUM

**Submitted**

**by**


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## SYNOPSIS

Metal corrosion processes can be controlled by different methods such as the modification of the corrosive medium or the metal and the use of protective agents. Protective agents act like corrosion inhibitors and they can be a single substance or a mixture that, when present on the surface in a specific concentration, can reduce or eliminate the corrosion process. Corrosion is the most serious and complex problem of the industries. Corrosion is the damage of material resulting from exposure and interaction with the environment. The structural materials used are invariably metals, which are easily damaged by the corrosive environment, causing heavy loss.

Most inhibitors used are synthesized from cheap raw materials some are chosen from compounds having hetero atoms (N, S, O, and P) in their aromatic or long carbon chain. The efficiency of these inhibitors mainly depends on their ability to be adsorbed on the metal surface, which results with replacement of water molecules at the corroding surface.

In recent times, the use of polymers as corrosion inhibitors has attracted considerable attention. Polymers are used as corrosion inhibitors, because through their functional groups they form complexes with metal ions and on the metal surface these complexes occupy a large surface area, thereby blanketing the surface and protecting the metals from corrosive agents present in solution. Literature survey reveals that a wide range of polymeric compounds have been successfully investigated as potential inhibitors for the corrosion of metals in aggressive media. The successful use of homopolymers such as polyacrylamide, polyvinyl pyrollidone, polyacrylic acid, polyethyleneimine, polyaniline, polyvinylpyridine, polyvinylbipyridine, poly(4-vinylpyridine), and polyvinyl imidazoles as corrosion inhibitors have been widely examined. The use of copolymers such as styrene-maleic acid and maleic acid-styrene-acrylic ester terpolymer as inhibitors has also been reported.

The present investigation has been conducted using the water soluble Polyvinyl alcohol- selected Amino acid composites, Polyvinyl alcohol-Alanine (PVAALA), Polyvinyl alcohol-Valine (PVAVAL), Polyvinyl alcohol-Glutamine (PVAGLN), Polyvinyl alcohol-Glutamic acid (PVAGLU), Polyvinyl alcohol-Tyrosine

(PVATYR), Polyvinyl alcohol-Tryptophan (PVATRP) on mild steel corrosion in 1M HCl medium.

Ashassi-Sorkhabi *et al.,* (2006) reported effect of some water-soluble polymers on corrosion of iron and cadmium. They found that the hydroxy group of polyvinyl alcohol and polyethylene glycol could be bridge between the polymer and the surface of electrode and resulted in an inhibiting effect in the HCl solution. Polyvinyl alcohol (PVA) is a water-soluble poly hydroxyl polymer, used in practical applications because of its easy preparation, excellent chemical resistance and physical properties and it is completely biodegradable and cheap. It is known that polymers are adsorbed stronger than their monomer analogues, hence it is expected that polymers will be better corrosion inhibitors than the corresponding monomers. The improved performances of the oligo- or polymeric materials are ascribed to their multiple adsorption sites for bonding with the metal surface. Polymers provide two advantages: a single polymeric chain displaces many water molecules from the metal surface, thus making the process entropically favorable and the presence of multiple bonding sites make the desorption of the polymers a slower process. This makes the investigation of their inhibiting properties significant in the context of the current priorities to produce eco-friendly inhibitors.

Hence the present research work aims at establishing the effectiveness of the synthesized water soluble Polyvinyl alcohol- selected Amino acids as potential corrosion inhibitors in 1M HCl medium.

**OBJECTIVES**

1. To synthesize the water soluble polymer composites – PVA with Alanine, Valine, Tyrosine, Tryptophan, Glutamine and Glutamic acid.
2. To characterise the synthesised water soluble polymer composites.
3. To utilise the same as corrosion inhibitor for mild steel in acid medium
4. To test the effectiveness of the inhibitors by weight loss and electrochemical measurements.
5. To evolve a suitable adsorption isotherm model.
6. To analyse the mode of inhibition from electrochemical measurements.
7. To compare the inhibition efficiency by various techniques.
8. To arrive at a possible mechanism for the inhibition process.

9. To ascertain the adsorption of polymer on mild steel surface by surface analysis method.

**EXPERIMENTAL DESIGN:**

Investigation of the inhibitive action of water soluble Polyvinyl alcohol-selected Amino acid composites on the corrosion of mild steel has been carried out using the following studies and techniques.

**Selection of Sample:**

Mild steel is widely used in most of the chemical industries due to its low cost and easy availability for fabrication of various reaction vessels, tanks, pipes, etc. Since it suffers from severe corrosion in aggressive environments, it has to be protected.

A large sheet of cold rolled mild steel coupons with a chemical composition of carbon 0.106%, manganese 0.196%, silicon 0.006%, phosphous 0.027%, sulphur 0.016%, chromium 0.022%,molybdenum 0.003%, nickel 0.012%, and iron 99.612% was utilized for the present study. The mild steel samples, with an active surface of $1\times5$ $Cm^2$ with 2 mm thickness are used for weight loss studies and one $cm^2$ area was used as the working electrode for electrochemical measurements.

**Selection of Acid media:**

Hydrochloric acid is extensively used in industries, the most important fields of application being acid pickling, industrial acid cleaning, acid cleaning, acid descaling and oil well acidizing. Hence 1 M HCl was used for the present study

**Selection of the inhibitor – (PVA – selected Amino acid composites ) :**

Polyvinyl alcohol is a semicrystalline, water soluble, synthetic linear polymer containing abundant secondary alcoholic groups. Polyvinyl alcohol is one of the popular precursor polymer matrixes for the fabrication of environmentally friendly, biodegradable and water soluble biopolymers. Polyvinyl alcohol based composites find applications in a wide range of industries including textiles, chemical and food for coating, adhesives, emulsifiers, collodial stabilizers, film packaging etc. Most of the natural amino acids are alpha amino acids which contain carboxyl and amino groups bonded to the same carbon atom. Amino acids are non toxic, biodegradable, relatively cheap, completely soluble in aqueous media and easy to produce with purities greater than 99%. Amino acids were reported as eco-friendly and non- toxic corrosion inhibitors.

Synthesis of water soluble polymers are preferred as the available conducting polymers are insoluble in common solvents. This motivated us to carry out the present research work on synthesis and utilisation of PVA – Amino acid composites as corrosion inhibitors which are water soluble in nature.

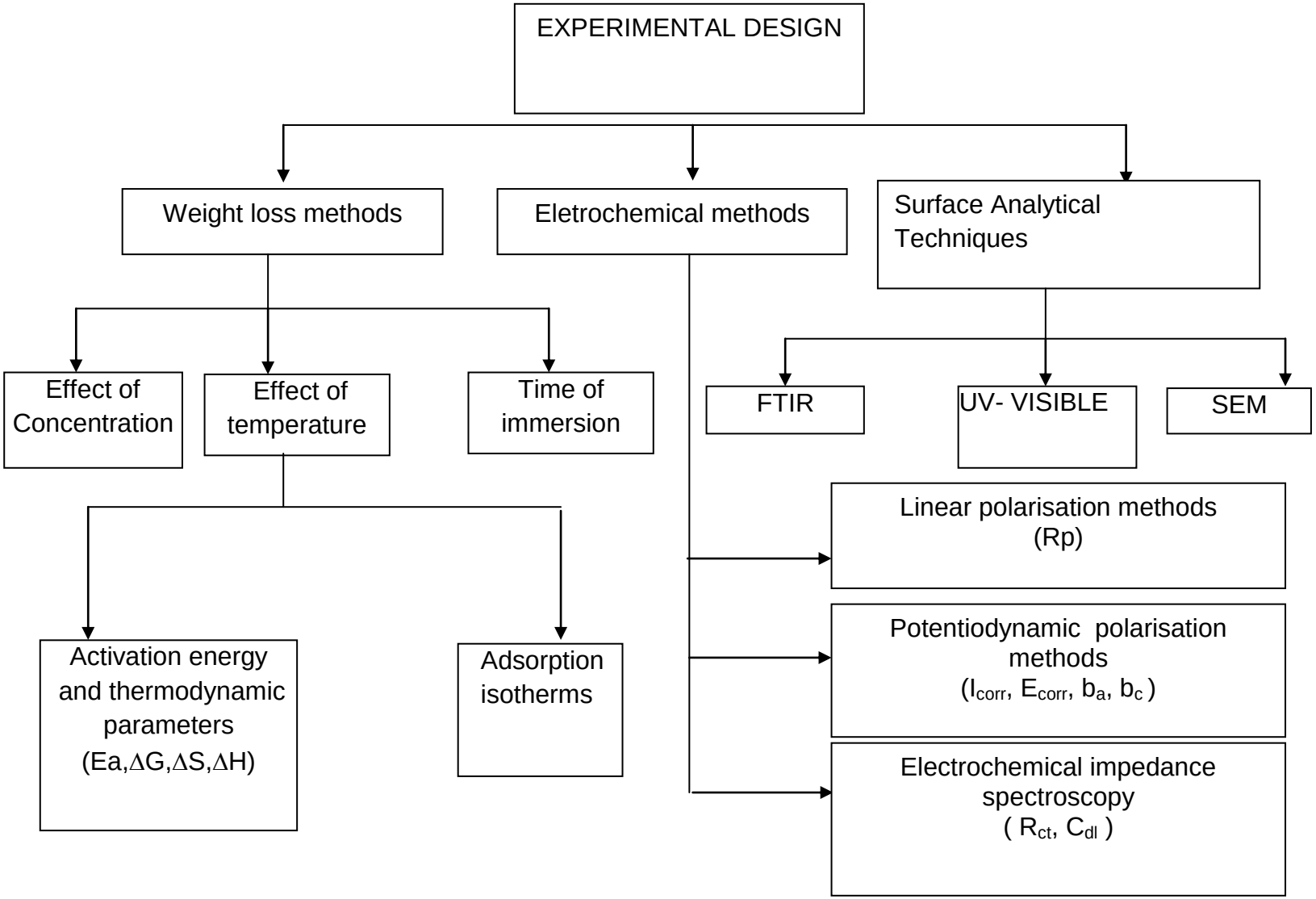
**Synthesis of the Inhibitors:**

The selected polymer composites undertaken for the present research work were synthesized using the standard procedure described by Trivedi, 1997, Gangopadhyay et.al., 2001, Mirmonseni and Wallace, 2003

**Characterization of synthesised water soluble Polyvinyl alcohol- selected Amino acid composites**

In order to confirm the chemical composition of the synthesized polymer composites, CHN analysis was carried out using the instrument **Vario EL CHNS serial number 11035060**. Conductivity measurement of compressed pellets of the polymer composites were carried out using the instrument **keithley (Four pourbe methods) and Solatron Electrochemical Analyzer**. TG/DTA and DSC were carried out using the instrument thermal analyzer **(SDTQ600V8.3build101**). The crystalline structure of the polymer composites was investigated using **XPERT-PRO X-ray diffractometer.** FTIR analysis was carried out using a **Bruker Tensor 27 FTIR** instrument **system IR spectrometer**. Aqueous solutions of PVA-Amino acids composites were subjected to UV-VIS Spectrophotometric characterization using **Aglient 8453 UV-Vis spectrophotometer**. Surface morphology of Polyvinyl alcohol- selected Amino acid composites were studied from **JOEL MODEL JSM 6360 Scanning Electron Microscope.**

**Techniques Adopted**



**Weight Loss measurements:**

Weight loss measurements were performed by immersing the mild steel coupons, in triplicate, into acid solution (100 mL) without and with the inhibitors at different periods of immersion. After the elapsed time, the specimen were taken out, washed, dried and weighed accurately. Weight loss experiments were done according to ASTM standard procedure.

**Electrochemical measurements:**

Electrochemical studies were carried out using Solatron electrochemical analyzer (model 1280 B) interfaced with an IBM computer. The experiments were performed as per the ASTM, G 1-72 standard procedure.

**Surface analytical techniques:**

Surface examination of the iron substrate in the presence and absence of the inhibitor was carried out by **Scanning Electron Microscope**. The interaction between the organic molecules and the metal surface has been studied by **FTIR spectra. UV-Visible spectrophotometer** was used to confirm the possibility of the Fe-complex formation on mild steel surface.

**Salient features:**

The salient features pertaining to the present study entitled **"**Synthesis, characterisation and utilisation of water soluble Polyvinyl alcohol- selected Amino acid composites as corrosion inhibitors for mild steel in acid medium**"** are summarized below:

1. Synthesised polymer composites were confirmed with the help of FTIR , UV VIS,TGA –DTA,DSC,XRD,SEM-EDX Analysis.
2. The investigated inhibitors, performed in an effective manner to minimize the corrosion of mild steel in HCl medium.
3. Analysis of the results of the weight loss measurement infers that the inhibition efficiency increased with increasing concentration of the water soluble Polyvinyl alcohol- selected Amino acid composites.
4. The inhibitors could furnish the following efficiency at a maximum concentration of 0.6% – 93.4% (6 hrs) in the presence of PVAALA, 95% (6 hrs) in the presence of PVAVAL, 95.5 %( 6 hrs) in PVAGLU, 94.4% (6 hrs) in PVAGLN, 96.8% (12 hrs) in PVATYR, 94.6% (3 hrs) in PVATRP respectively.

5. Immersion studies results reveal that as the time of immersion increased from ½ hr to 6 hrs the inhibition efficiency increased. After 6 hrs there was a slight decline in the inhibition efficiency at 12 hrs and 48 hrs for all the investigated polymer composites. The decrease in inhibition efficiency at longer immersion time may be due to the desorption of the protective layer formed in the presence of the water soluble Polyvinyl alcohol-selected amino acids composites on the mild steel surface. All the investigated inhibitors could furnish efficiency 90-95% at 3 hrs of immersion.
6. All the examined inhibitors reveal that inhibition efficiency increased with increase in particular temperature and then decreased at higher temperatures. Maximum IE for all investigated inhibitors were found to be around 90%. This may be due to the adsorption of the inhibitor upto particular temperature and then desorption of the inhibitor at higher temperature.
7. In the present investigation Ea values are found to be greater or smaller than those calculated in the presence of the inhibitors. This can be explained by the fact that at high degree of coverage, the dissolution process is not only determined by the reaction of the metal from the bare surface but also involves the adsorbed inhibitor.
8. The negative value of $\Delta G^{o}_{ads}$ indicate that the inhibitor is spontaneously adsorbed onto the metal surface. In the present study, the calculated values of $\Delta G^{o}_{ads}$ obtained for the investigated system ranges between -10 kJ/mole to -25 kJ/mole indicating that the adsorption of the inhibitors on the surface of the mild steel may be a combination of physisorption and chemisorption (comprehensive adsorption). The negative sign of $\Delta H^{o}_{ads}$ indicated that the adsorption of water soluble Polyvinyl alcohol- selected Amino acid composites on the mild steel surface is exothermic in nature. The values of entropy of adsorption are also negative. Inspection of water soluble Polyvinyl alcohol- selected Amino acid composites revealed that decrease in enthalpy and entropy are the driving force for the adsorption on the mild steel surface.
9. The $E_{corr}$ for all the examined inhibitor systems in HCl acid medium do not change appreciably with the addition of the inhibitors and thus affect the anodic dissolution as well as cathodic hydrogen evolution reactions and act as mixed type inhibitors.

10. $I_{corr}$ values decrease significantly in the presence of inhibitors showing that all the inhibitors are effective in controlling corrosion.
11. The anodic and cathodic tafel slopes $b_a$ and $b_c$ shifted to a higher potential region in the presence of inhibitors. Appreciable shift of cathodic and anodic polarization curves is an indication of mixed type behaviour of the inhibitors.
12. $R_p$ values increases with increase in inhibitor concentration indicating a better corrosion protective ability of the inhibitors under study.
13. The Nyquist plots contain depressed semi-circles with the centre under the real axis, whose size increases with the increase in water soluble Polyvinyl alcohol-selected Amino acid composites concentration, indicating a charge transfer process which mainly controls the corrosion of mild steel. The impedance parameter $R_{ct}$ for the corrosion of mild steel in acid medium with the addition of various concentrations of water soluble Polyvinyl alcohol- selected Amino acid composites increased with increasing concentration of the inhibitors. $C_{dl}$ values tended to decrease in the presence of the inhibitor. This behaviour revealed the adsorption of Polyvinyl alcohol- selected Amino acid composites on mild steel.
14. The morphology of the specimen surface using SEM revealed a corroded rough and coarse uneven surface in the absence of the inhibitor. However in the presence of the inhibitors smooth surface of the specimen was observed due to the suppression of the corrosion rate.
15. From the IR spectral data, it has been found that the peaks for -OH, -NH2, -COOH and aliphatic and aromatic C-H stretching disappear thus proving that the adsorption takes place through oxygen, nitrogen and aromatic ring atoms. UV spectra confirmed the possibility of the formation of water soluble Polyvinyl alcohol- selected Amino acid composites-Fe complex.
16. From the experimental findings it is understood that PVA-Amino acids composites are physically and chemically adsorbed due to the donor atoms N and O of inhibitors and vacant‘d’ orbitals of iron surface atoms. Furthermore, PVA-Amino acids composites molecules are large and flat enough to block more surface areas of mild steel. The PVA- selected Amino acid composite molecule can also co-ordinately bond with the metal. The inhibitor molecules can also be adsorbed on the metal surface in the form of negative charged species which can interact electrostatically with positively charged metal surface.

17. Experiments performed with PVA, AA individually for 3 hrs immersion studies reveal IE of 80 % and 55 % whereas the PVA – selected Amino acid composites could furnish an efficiency of 90 %.
18. This study justifies the utilisation of the PVA – selected Amino acid composites as corrosion inhibitors.

**CONCLUSION**

- Water soluble Polyvinyl alcohol- selected Amino acid composites acts as potential benign inhibitors for the corrosion of mild steel in 1M hydrochloric acid.
- The inhibition efficiency increased with increase in concentration of the inhibitors.
- The adsorption of the inhibitors obeys Langmuir adsorption isotherms.
- Thermodynamic parameters confirms the strong interaction of the inhibitors with the mild steel surface
- Tafel studies, linear polarization and impedance studies revealed that the inhibitors act as mixed type inhibitors.
- FTIR & UV-Visible spectroscopic studies confirm the formation of PVA- Amino acids composites -Fe complex.
- SEM studies prove the adsorption of the PVA- Amino acids composites on the mild steel surface.

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